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(54) **Insecticidally active nitro compounds.**

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**EP-A- 0 104 423**
**EP-A- 0 163 855**
**EP-A- 0 302 389**

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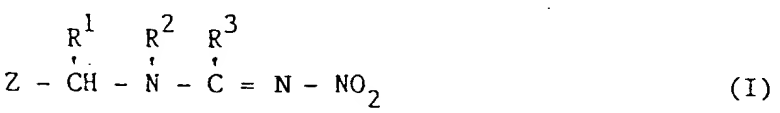
## Description

The present invention relates to novel nitro compounds, to processes for their preparation and to their use as insecticides.

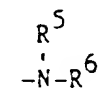
It has already been disclosed that a certain group of 2-nitro-1,1-ethenediamines is useful as medicaments which influence the circulation, in particular as hypotensive agents (see US-A- 4,567,188 corresponding to EP-A- 104423), a certain group of N-cyanoisothioureas is useful as medicaments for treating ulcers (see Japanese Patent Laid-open No. 234,064/1987), the N-cyanoisothioureas disclosed in the above Japanese patent application have also a function for controlling insects and plant-destructive nematodes (see Japanese Patent Laid-open No. 233,903 and EP-A 303,570), and that a certain group of $\alpha$-unsaturated amines has insecticidal/miticidal activity (see EP-A 0302389). EP-A- 375907 is an earlier application to which the disclaimers of claims 1-5 refer to.

There have now been found novel nitro compounds of the formula (I)

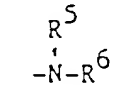


(I)

wherein $R^1$ is hydrogen, methyl, ethyl or n-propyl;
$R^2$ is hydrogen, $C_{1-4}$-alkyl, allyl, propargyl, $C_{3-6}$-cycloalkyl optionally substituted by methyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen, $C_{1-3}$-alkoxy or - $CH_2$- $Z^1$ in which
$Z^1$ is pyridyl optionally substituted by halogen;
$R^3$ is -O-$R^4$, -S-$R^4$ or



in which
$R^4$ is $C_{1-4}$ alkyl, allyl, $C_{3-6}$ cycloalkyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen or -$CH_2$-$Z^1$ in which $Z^1$ has the same meaning as stated above;
$R^5$ and $R^6$ are hydrogen, $C_{1-6}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino, methylamino, dimethylamino, methoxycarbonyl and cyano, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, $C_{1-3}$ alkoxy, hydroxy, formyl,
$C_{1-3}$ alkylamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, pyridyl optionally substituted by chlorine or methyl, or -$CH_2$-$Z^2$ in which $Z^2$ represents the definition of $Z^1$ hereinbefore and 5-thiazolyl optionally substituted by chlorine, in addition $R^5$ and $R^6$ may form, together with the adjacent nitrogen atom, a 3 to 6 membered cyclic group which may be substituted by methyl and may have an N, O or S atom as said ring member besides the adjacent nitrogen atom;
and
Z is a 5-membered heterocyclic group which has one or two-nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom and may be substituted by halogen or $C_{1-4}$ alkyl, or a 6-membered heterocyclic group which has one or two nitrogen atoms and may be substituted by halogen or $C_{1-4}$ alkyl optionally substituted by halogen with the exception of the case where $R^1$ is hydrogen, methyl, ethyl or n-propyl, $R^2$ is hydrogen or $C_{1-4}$ alkyl, $R^3$ is -S-$R^4$ or



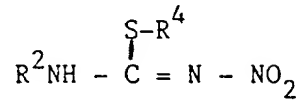
in which $R^4$ is $C_{1-4}$ alkyl, $R^5$ and $R^6$ are hydrogen or $C_{1-4}$ alkyl, and Z is 5- or 6-membered heterocyclic group having at least one nitrogen atom which may be substituted by halogen or $C_{1-4}$ alkyl optionally

substituted by halogen.

The compounds of the formula (I) can be obtained by a process in which

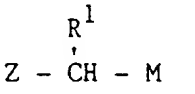
a): (in the case where $R^3$ is -S-$R^4$)

compounds of the formula (VI)



(VI)

wherein $R^2$ and $R^4$ have the same meanings as mentioned above, are reacted with compounds of the formula (VII)



(VII)

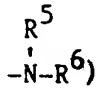
wherein $R^1$ and Z have the same meanings as mentioned above,

and M is halogen, methanesulfonyloxy or tosyloxy,

in the presence of inert solvents, and if appropriate in the presence of acid binders,

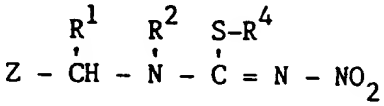
or

b): (in the case where $R^3$ is



)

compounds of the formula (Id)



(Id)

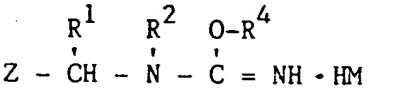
wherein $R^1$, $R^2$, $R^4$ and Z have the same meanings as mentioned above,

are reacted with the aforementioned compounds of the formula (IV) in the presence of inert solvents,

or

c): (in the case where $R^3$ is -O-$R^4$)

compounds of the formula (VIII)



(VIII)

wherein $R^1$, $R^2$, $R^4$, Z and M have the same meanings as mentioned above,

are reacted with fuming nitric acid in the presence of concentrated sulfuric acid, and if appropriate in the presence of inert solvents,

The novel nitro compounds exhibit powerful insecticidal properties.

Surprisingly, the nitro compounds according to the invention exhibit a substantially greater insecticidal action than those known from the above cited prior arts.

Preferred nitro compounds of the formula (I) are those in which
$R^1$ is hydrogen, methyl or ethyl;
$R^2$ is hydrogen, methyl, ethyl, n-propyl, allyl, propargyl, cyclohexyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, $C_{1-2}$ alkoxy or
2-chloro-5-pyridylmethyl;
$R^3$ is

in which $R^5$ and $R^6$ are hydrogen, $C_{1-4}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino, methylamino, dimethylamino, methoxycarbonyl and cyano, allyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, $C_{1-2}$ alkoxy, hydroxy, formyl, $C_{1-2}$ alkylamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, 2-chloro-5-pyridyl, 2-chloro-5-pyridylmethyl or 2-chloro-5-thiazolylmethyl, in addition $R^5$ and $R^6$ may represent, together with the adjacent nitrogen atom, pyrrolidino, piperidino, 2-methylpiperidino, morpholino, piperazino or 1-isoxazolyl;
and
Z is 5-membered heterocyclic group which has one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom and may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine, or 6-membered heterocyclic group which has one or two nitrogen atoms and may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine;
with the exception of the case
where $R^1$ is hydrogen, methyl or ethyl,
$R^2$is hydrogen, methyl, ethyl or n-propyl,
$R^3$ is

in which $R^5$ and $R^6$ are hydrogen or $C_{1-4}$ alkyl,
and Z is 5- or 6-memered heterocyclic group having at least one nitrogen atom which may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine.

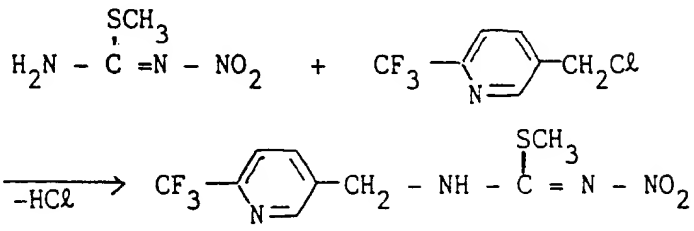
Very particularly preferred nitro compounds of the formula (I) are those in which
$R^1$ is hydrogen or methyl;
$R^2$ is hydrogen, methyl, ethyl, allyl, propargyl, methoxy or 2-chloro-5-pyridylmethyl;
$R^3$ is

in which $R^5$ and $R^6$ are hydrogen, $C_{1-2}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino, methylamino, dimethylamino, methoxycarbonyl and cyano, allyl, 2-chloroallyl, benzyl, 3- or 4-chlorobenzyl, methoxy, hydroxy, formyl, methyamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, 2-chloro-5-pyridyl or 2-chloro-5-pyridylmethyl;
and
Z is 2-chloro-5-pyridyl;
with the exception of the case where $R^1$ is hydrogen or methyl,
$R^2$ is hydrogen, methyl or ethyl,
$R^3$ is

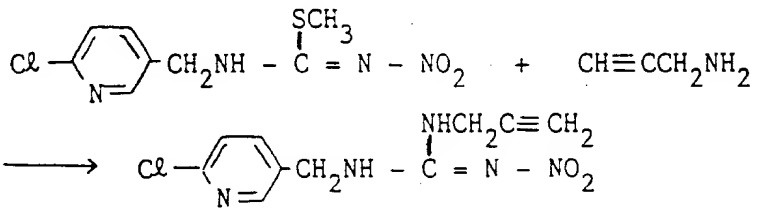
in which $R^5$ and $R^6$ are hydrogen
or $C_{1-2}$ alkyl, Y is N, and Z is 2-chloro-5-pyridyl.

Specifically, the following compounds may be mentioned:
1-allyl-3-(-2-chloro-5-pyridylmethyl)-2-nitroguanidine, and
1,3-bis-(2-chloro-5-pyridylmethyl)-2-nitroguanidine.

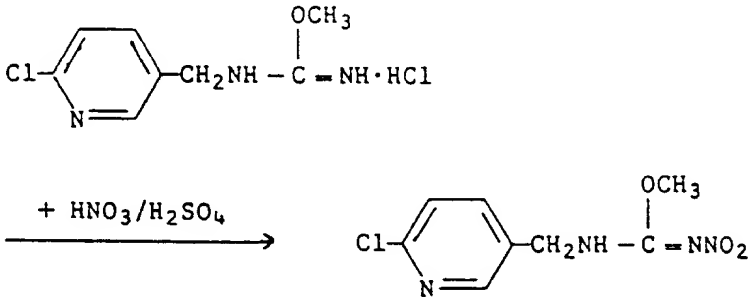
If, for example, in the above process a),
3-nitro-2-methylisothiourea and 5-chloromethyl-2-trifluoromethylpyridine are used as starting materials, the course of the reaction can be represented by the following equation:



If, for example, in the above process b),
1-(2-chloro-5-pyridylmethyl)-3-nitro-2-methylisothiourea and propargylamine are used as starting materials, the course of the reaction can be represented by the following equation:



If, for example, in the above process c),
1-(2-chloro-5-pyridylmethyl)-2-methylisourea is used as a starting material, the course of the reaction can be represented by the following equation:



In the process a) the compounds of the formula (VI) as a starting material are those based on the aforementioned definitions of $R^2$ and $R^4$.

In the formula (VI), $R^2$ and $R^4$ preferably have the meanings already given above.

The compounds of the formula (VI) are known (see e.g. J. Am. Chem. Soc., vol. 76, pages 1877 - 1879, 1954), and as examples, there may be mentioned:
3-nitro-2-methylisothiourea, 1,2-dimethyl-3-nitroisothiourea or 1,1,2-trimethyl-3-nitroisothiourea.

The compounds of the formula (VII) as a starting material are those based on the aforementioned definitions of $R^1$, Z and M.

In the formula (VII), $R^1$ and Z have the meanings already given above, and M represents chlorine, bromine or tosyloxy.

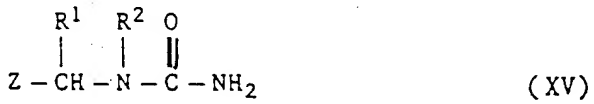
The compounds of the formula (VII) include known compounds (see Japanese Patent Laid-open Nos. 178,981/1986, 178,982/1986 or 183,271/1986), and as examples, there may be mentioned:
2-chloro-5-chloromethylpyridine,
2-chloro-5-chloromethylthiazole or
5-chloromethyl-2-trifluoromethylpyridine.

In the process b), the compounds of the formula (Id) are a part of the compounds of the formula (I) which can be prepared by the above process a).

In the process c), the compounds of the formula (VIII) as a starting material are those based on the aforementioned definitions of $R^1$, $R^2$, $R^4$, Z and M.

In the formula (VIII), $R^1$, $R^2$, $R^4$, Z and M have the meanings already given above.

The compounds of the formula (VIII) are novel and in general, can be obtained when compounds of the formula (XV)



(XV)

wherein $R^1$, $R^2$ and Z have the same meanings as mentioned above, are reacted with compounds of the formula (XIV)

$R^4$ - M (XIV)

wherein $R^4$ and M have the same meanings as mentioned above.

The above compounds of the formula (XV) in general can be obtained when the aforementioned compounds of the formula (III) are reacted with urea.

The above compounds of the formula (XVI) are well-known in the field of organic chemistry, and as examples there may be mentioned:
methyl, ethyl, n-propyl, iso-propyl and 3-pyridylmethyl esters of p-toluene-sulfonic acid, and monochlorides of methane, ethane and propane.

As examples of the compounds of the formula (XV), there may be mentioned: 1-(2-chloro-5-pyridylmethyl)urea, 1-(2-chloro-5-thiazolyl)urea, 1-(2-chloro-5-pyridyl)-1-methylurea or
1-[1-(2-chloro-5-pyridyl)ethyl]urea.

As examples of the compounds of the formula (VIII), there may be mentioned:
hydrochloride or p-toluenesulfonate of 1-(2-chloro-5-pyridylmethyl)-2-methylisourea,
hydrochloride of 1-(2-chloro-5-pyridylmethyl)-2-methylisourea, or p-toluene-sulfonate thereof,
hydrochloride of 1-(2-chloro-5-thiazolylmethyl)-2-methylisourea, or p-toluene-sulfonate.

Suitable diluents in the process a) are all inert solvents.

These preferentially include water; aliphatic-, cycloaliphatic- and aromatic- hydrocarbons optionally chlorinated such as hexane, cyclohexane, petroleum ether, ligroin, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, trichloroethylene or chlorobenzene; ethers such as diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, propylene oxide, dioxane or tetrahydrofuran; ketones such as acetone, methylethyl ketone, methyl-iso-propyl ketone, methyl-iso-butyl ketone; nitriles such as acetonitrile, propionitrile or acrylonitrile; alcohols such as methanol, ethanol, isopropanol, butanol or ethylene glycol; esters such as ethyl acetate, amyl acetate; acid amides such as dimethyl formamide or dimethyl acetamide; and sulfones and sulfoxides such as dimethyl sulfoxide or sulfolane; and bases, for example, such as pyridine.

The process a) may be carried out in the presence of acid binders, such as hydroxide, hydride, carbonate, bicarbonate and alcolate of alkali metal, and tertiary amines, for examples, triethylamine and diethylaniline, and pyridene.

In the process a), the reaction temperature can be varied within a wide range. For example, the reaction is carried out at a temperature in the range of from 0 °C to boiling point of the reaction mixture, preferably from 0 °C to 80 °C.

In general, the reaction is preferably carried out under normal pressure; and also elevated or reduced pressure.

In carrying out the process a), for instance,equi-molar to 1.2 mole, preferably equi-molar to 1.1 mole amount of the compounds of the formula (VII) may be employed per mole of the compounds of the formula (VI), and the mixture is reacted in the presence of inert solvents, for example, dimethylsulfoxide and in the presence of a base, sodium hydride, so that the desired compounds of the formula (I) can be obtained.

In carrying out the process b), suitable diluents include the same solvents as exemplified for the process a).

In the process b), the reaction temperature can be varied within a wide range. For example, the reaction is carried out at a temperature in the range of from 0 °C to 150 °C, preferably from 20 °C to 90 °C.

In general, the reaction is preferably carried out under normal pressure, and also elevated or reduced pressure.

In carrying out the process b), for instance,equi-molar to slightly excessive molar amount of the compounds of the formula (IV) may be employed per mole of the compounds of the formula (Id), and the mixture is reacted in the presence of inert solvents, so that the desired compounds of the formula (I) can be obtained.

In carrying out the process c), for instance, the compounds of the formula (VIII) which is dissolved in concentrated sulfuric acid are reacted with fuming nitric acid having a purity of higher than 98% at a low temperature, preferably at 0 °C or less than 0 °C, so that the desired compounds of the formula (I) can be obtained.

The compounds are well tolerated by plants, have a favourable level of toxicity to warm-blooded animals, and can be used for combating arthropod pests, especially insects which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The above-mentioned pests include:

from the class of the Isopoda, for example Oniscus Asellus, Armadillidium vulgare and Porcellio scaber;

from the class of the Diplopoda, for example Blaniulus guttulatus;

from the class of the Chilopoda, for example Geopililus carpophagus and Scutigera spec.;

from the class of the Symphyla, for example Scutigerella immaculata;

from the order of the Thysanura, for example Lepisma saccharina;

from the order of the Collembola, for example Onychirus armatus;

from the order of the Orthoptera; for example Blatta orientails, Periplaneta americana, Leucophaea maderae, Blattella germanica, Acheta domesticus, Gryllotalpa spp., Locusta migrato ria migratorioides, Melanoplus differentialis and Schistocerca gregaria;

from the order of the Dermaptera, for example Forficula auricularia;

from the order of the Isoptera, for example Reticulitermes spp.;

from the order of the Anoplura, for example Phylloxera vastatrix, Pemphigus spp., Pediculus humanus corporis, Haematopinus spp. and Linognathus spp.;

from the order of the Mallophaga, for example Trichodectes spp. and Damalinea spp.;

from the order of the Thysanoptera, for example Hercinothrips femoralis and Thrips tabaci,

from the order of the Heteroptera, for example Eurygaster spp., Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus and Triatoma spp.;

from the order of the Homoptera, for example Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Aphis fabae, Doralis pomi, Erisoma lanigerum, Hyalopterus arundinis, Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantti, Aspidiotus hederae, Pseudococcus spp. and Psylla spp.;

from the order of the Lepidoptera, for example Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponometua padella, Plutella maculipennis, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp., Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Spodoptera exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Spodoptera spp., Trichoplusia ni, Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiquella, Homona magnanima and Tortrix viridana;

from the order of the Coleoptera, for example Anobium punctatum, Rhizopertha dominica, Acanthoscelides obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthononmus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis and Costelytra zealandica;

from the order of the Hymenoptera for example Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis and Vespa spp.;

from the order of the Diptera, for example Aedes spp., Anopheles spp., Culex spp, Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomyia spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae and Tipula paludosa;

from the order of the Siphonaptera, for example Xenopsylla cheopis and Ceratophyllus spp.;

from the class of the Arachnida, for example Scorpio maurus and Latrodectus mactans;

from the order of the Aranina, for example Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp. and Tetranychus spp..

The plant-parasitic nematodes include Pratylenchus spp., Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp., and Trichodorus spp..

Furthermore, in the field of veterinary medicine, the novel compound of the present invention can effectively be employed for combating a variety of noxious animal-parasitic pests (internal- and external-parasitic pests), e.g.,parasitic insects and nematodes. Such animal-parasitic pests may be exemplified as follows:

From the class of insects, e.g., Gastrophilus spp., Stomoxys spp., Tricodectes spp., Rhodius spp., Ctenocephalides canis and the like.

The compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, coating compositions for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations can be produced in known manner, for example by mixing the active compounds with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid solvents diluents or carriers, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene or alkyl napthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethyl-sulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates. As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-tonic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products.

Dispersing agents include, for example, lignin sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulation.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent by weight.

The active compounds according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilising agents, acaricides, nematicides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phospahtes, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas, substances produced by microorganisms.

The active compounds according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agent are compounds which increase the action of the active compounds, without it being necessary for the synergistic agent added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 100% by weight of active compound, preferably between 0.0001 and 1% by weight.

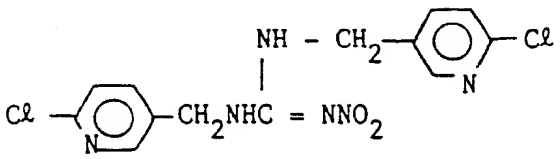
The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

The preparation and use of the active compounds according to the invention can be seen from the following examples.

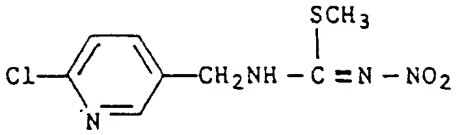
Preparative examples:

Example 1



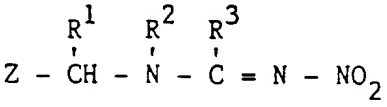
1-2-(chloro-5-pyridylmethyl)-2-methyl-3-nitroisothiourea (1.0 g) was dissolved in ethanol ( 20 ml) and to the solution was added 2-chloro-5-aminomethylpyridine (0.55 g) at room temperature, followed by one day stirring at 30 °C. The ethanol in the solution was distilled off under reduced pressure and it was purified on a chromatographic column (the eluent was a mixture of methanol and chloroform) so as to obtain the desired 1,3-bis-(2-chloro-5-pyridylmethyl)-2-nitroguanidine (1.0 g) having a melting point in the range of from 179 to 182 °C.

Referential Example 1



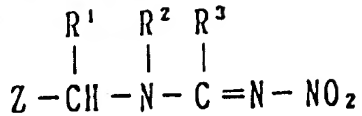
To a solution of 2-methyl-3-nitroisothiourea (15.0 g) in dimethylsulfoxide (100 ml) was gradually added sodium hydride (oil free 2.9 g) at 5 °C, while being stirred for one hour. Thereafter, 2-chloro-5-chloromethyl pyridine (18.0 g) was added to the solution at a temperature in the range of from 5 to 10 °C, followed by an overnight stirring thereof at room temperature. After the dimethylsulfoxide in the solution having been distilled off under reduced pressure, the resulting residue was purified on a chromatographic column (the eluent was a mixture of ethanol and chloroform), so as to obtain the desired 1-(2-chloro-5-pyridylmethyl)-2-methyl-3-nitroisothiourea (2.0 g) having a melting point in the range of from 141 to 143 °C.

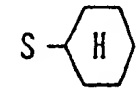
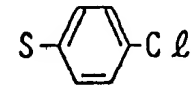
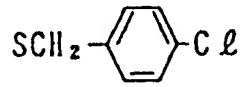
The compounds of the following formula (I),



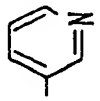
which can be prepared in the same way as in the above Example 1 and Referential Example 1 are shown in Table 1.

Table 1

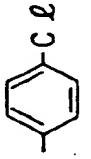
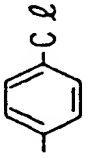
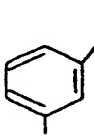
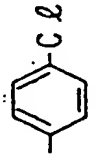


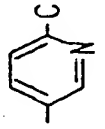
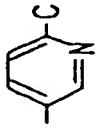
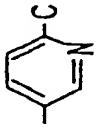
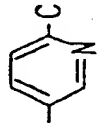
| Comp. No. | Z | $R^1$ | $R^2$ | $R^3$ | |
|---|---|---|---|---|---|
| 1 | 2-trifluoromethyl-5-pyridyl | $C_2H_5$ | H | $SCH_3$ | |
| 2 | 2,3-dichloro-5-pyridyl | H | H |  | |
| 3 | 3-methyl-5-isoxazolyl | H | H |  | |
| 4 | 2-chloro-5-thiazolyl | H | $C_2H_5$ |  | |

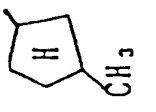
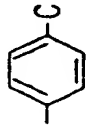
| Comp. No. | Z | $R^1$ | $R^2$ | $R^3$ | |
|---|---|---|---|---|---|
| 5 | 2-chloro-5-thiazolyl | H | H | $OCH_3$ | |
| 6 | 2-chloro-5-pyridyl | H | H | $OCH_3$ | |
| 7 | 2-chloro-5-pyridyl | H | $CH_3$ | $OCH_3$ | |
| 8 | 2-methyl-1,3,4-oxadiazol-5-yl | H | H | $OCH_3$ | |
| 9 | 1,2,5-thiadiazol-3-yl | H | H | $OCH_3$ | |
| 10 | 3-methyl-5-isoxazolyl | $CH_3$ | H | $OC_2H_5$ | |
| 11 | 2-chloro-5-thiazolyl | H | H | $OC_3H_{7-n}$ | |
| 12 | 1,2,5-thiadiazol | H | H | $OC_3H_{7-iso}$ | |

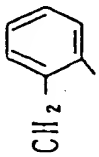
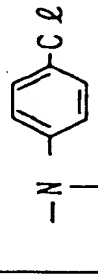
| Comp. No. | Z | $R^1$ | $R^2$ | $R^3$ | |
|---|---|---|---|---|---|
| 13 | 2-pyrazinyl | $C_3H_{7-n}$ | H |  | |
| 14 | 2-chloro-5-pyridyl | H | $CH_2C\equiv CH$ | $-NHCH_3$ | |
| 15 | 2-cyano-5-pyridyl | H | $CH_3$ | $-NHC_2H_5$ | |
| 16 | 2-chloro-5-thiazolyl | H | H | $-NHCH_2CC\ell=CH_2$ | |
| 17 | 2-methyl-5-pyridyl | H | $CH_3$ | $-NHCH_2CC\ell=CH_2$ | |
| 18 | 2-chloro-5-pyridyl | H | H | $-NHCH_2CH=CH_2$ | |
| 19 | 2-chloro-5-pyridyl | H | $CH_3$ | $-NHCH_2CH=CH_2$ | |

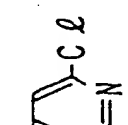
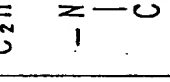
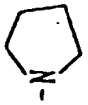
| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 20 | 2-methyl-5-pyrazinyl | H | $CH_3$ | $-NHCH_2CH=CH_2$ | |
| 21 | 2-chloro-5-pyridyl | H | H | $-NHCH_2C\equiv CH$ | $n_D^{50}$ 1.15955 |
| 22 | 2-chloro-5-pyridyl | H | $CH_3$ | $-NHCH_2C\equiv CH$ | |
| 23 | 2-chloro-5-pyridyl | H | H |  | |
| 24 | 2-chloro-5-pyridyl | H | $CH_3$ |  | |
| 25 | 2-chloro-5-thiazolyl | H | $CH_3$ |  | |
| 26 | 2-methyl-5-pyrazinyl | H | $CH_3$ |  | |

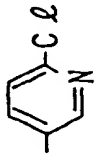
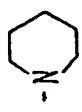
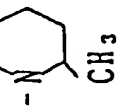
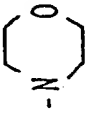
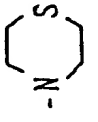
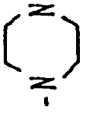
| Comp. No. | Z | R¹ | R² | R³ |
|---|---|---|---|---|
| 27 | 2-chloro-5-pyridyl | H | H |  |
| 28 | 2-chloro-5-pyridyl | H | $CH_3$ |  |
| 29 | 2-chloro-5-pyridyl | H | H |  |
| 30 | 2-chloro-5-pyridyl | H | $CH_3$ |  |
| 31 | 2-chloro-5-pyridyl | H | $CH_3$ |  |
| 32 | 1,2,5-thiadiazol-3-yl | H | H |  |

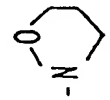
| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 33 | 2-chloro-5-pyridyl | H | H |  | mp.179~182 °C |
| 34 | 2-chloro-5-pyridyl | H | $CH_3$ |  | |
| 35 | 2-chloro-5-pyridyl | H | H |  | |
| 36 | 2-chloro-5-pyridyl | H | $CH_3$ |  | |

| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 37 | 2,3-dichloro-5-pyridyl | H |  | $-N(CH_3)_2$ | |
| 38 | 2-chloro-5-pyridyl | H | $CH_2C{\equiv}CH$ | $-N(CH_3)_2$ | |
| 39 | 2,3-dimethyl-5-pyridyl | H |  | $-N(C_2H_5)(CH_3)$ | |
| 40 | 2-chloro-5-pyridyl | H | H | $-N(CH_2CH{=}CH_2)(CH_3)$ | |
| 41 | 2-chloro-5-pyridyl | H | H | $-N(CH_2CH{=}CH_2)(CH_3)$ | |

| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 42 | 2-chloro-5-pyridyl | H |  |  | |
| 43 | 2-methyl-5-pyrazinyl | H | H |  | |
| 44 | 2-methyl-5-pyridyl | H | H |  | |
| 45 | 2-bromo-5-pyridyl | H | H |  | |

| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 46 | 2-chloro-5-pyrimidinyl | H | H |  | |
| 47 | 2-fluoro-5-thiazolyl | H |  |  | |
| 48 | 1,2,5-oxadiazol-3-yl | H | H |  | |
| 49 | 2-chloro-5-pyridyl | H | H |  | mp.169~172 °C |

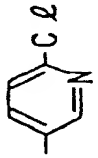
| Comp. No. | Z | $R^1$ | $R^2$ | $R^3$ | |
|---|---|---|---|---|---|
| 50 | 2-chloro-5-pyridyl | $CH_3$ |  |  | |
| 51 | 2-chloro-5-pyridyl | H | H |  | |
| 52 | 2-chloro-5-pyridyl | H | H |  | |
| 53 | 2-chloro-5-pyridyl | H | H |  | |
| 54 | 2-chloro-5-pyridyl | H | H |  | |
| 55 | 2-chloro-5-pyridyl | H | H |  | |

| Comp. No. | Z | R' | R² | R³ | |
|---|---|---|---|---|---|
| 56 | 2-chloro-5-pyridyl | H | $CH_3$ |  | |
| 57 | 2-chloro-5-pyridyl | H | H | $NHOCH_3$ | |
| 58 | 2-chloro-5-pyridyl | H | $CH_3$ | $NHOCH_3$ | |
| 59 | 2-chloro-5-pyridyl | H | H | $N(CH_3)OCH_3$ | |
| 60 | 2-chloro-5-pyridyl | H | $CH_3$ | $N(CH_3)OCH_3$ | |

| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 61 | 2-chloro-5-pyridyl | H | H | $NHNH_2$ | |
| 62 | 2-chloro-5-pyridyl | H | H | $NHNHCH_3$ | |
| 63 | 2-chloro-5-thiazolyl | H | H | $NHNHCH_3$ | |
| 64 | 2-chloro-5-thiazolyl | H | $CH_3$ | $NHN(CH_3)_2$ | |
| 65 | 2-chloro-5-pyridyl | H | H | NHOH | |
| 66 | 2-chloro-5-pyridyl | H | $CH_3$ | NHOH | |

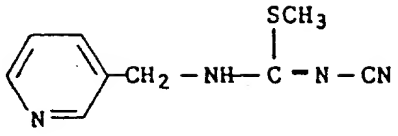
| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 67 | 2-chloro-5-pyridyl | H | H | $NHCH_2CH_2OC_2H_5$ | |
| 68 | 2-chloro-5-thiazolyl | H | H | $NHCH_2CH_2SH$ | |
| 69 | 2-chloro-5-pyridyl | H | H | $NHCH_2CH_2NH_2$ | |

| Comp. No. | Z | R¹ | R² | R³ | |
|---|---|---|---|---|---|
| 70 | 2-bromo-5-thienyl | H | $CH_3$ | $NH_2$ | mp.159~161 °C |
| 71 | 2-bromo-5-thienyl | H | $CH_3$ | $NHCH_3$ | |
| 72 | 2-bromo-5-thienyl | H | $CH_3$ | $N(CH_3)_2$ | |
| 73 | 2-bromo-5-thienyl | H | H | $NHCH_3$ | |
| 74 | 2-chloro-5-pyridyl | H | $CH_3$ | N-CHO<br>\|<br>$CH_3$ | mp. 99~101 °C |

| Comp. No. | Z | R¹ | R² | R³ |
|---|---|---|---|---|
| 75 | 2-chloro-5-pyridyl | H | H | $NHCOCH_3$ |
| 76 | 2-chloro-5-pyridyl | H | $CH_3$ | $NHCOCH_3$ |
| 77 | 2-chloro-5-pyridyl | H | H |  |
| 78 | 2-chloro-5-pyridyl | H | $CH_3$ |  |

Biological tests

Comparative compound E-1



{ disclosed in Japanese Patent Laid-open No. 233903/1988 }

Example 5 (biological test)

Test on Mephotettix cinciticeps having resistance to organophosphorus agents:-

Preparation of a test chemical

Solvent: 3 parts by weight of xylene
Emulsifier: 1 part by weight of polyoxyethylene alkyl phenyl ether

To form a suitable preparation, 1 part by weight of the active compound was mixed with the aforesaid amount of the solvent containing the aforesaid amount of the emulsifier. The mixture was diluted with water to a predetermined concentration.

Testing method

Onto rice plants, about 10 cm tall, planted in pots each having a diameter of 12 cm was sprayed 10 ml per pot of the water-dilution of each active compound in a predetermined concentration prepared as above. The sprayed chemical was dried, and a wire net having a diameter of 7 cm and a height of 14 cm was put over each pot, and 30 female imagoes of Nephotettix cincticeps showing resistance to organophosphorus agents were released into the net. The pots were each placed in a constant temperature chamber and the number of dead insects was examined 2 days later, and the Insect mortality was calculated.

As the result, for instance, compound Nos. 21 and 35 showed 100% of kill ratio at 50 ppm active ingredient.

On the other hand, as comparison, E-1 showed no killing effect at 50 ppm a.i.

Example 6 (biological test)

Test on planthoppers:-

Testing method

A water dilution in a predetermined concentration of the active compound prepared as in Example 5 was sprayed onto rice plants, about 10 cm tall, grown in pots with a diameter of 12 cm in an amount of 10 ml per pot. The sprayed chemical was dried, and a wire net, 7 cm in diameter and 14 cm tall, was put over each of the pots. Thirty female imagoes of Nilaparvata lugens Stal of a strain which showed resistance to organophosphorus chemicals were released into the net. The pots were left to stand in a constant temperature chamber and the number of dead insects was examined two days later. The kill ratio was then calculated.

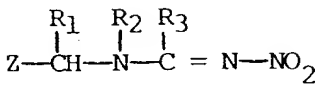
In the same way as above, the insect mortality was calculated on Sogatella furcifera Horvath and organophosphorus-resistant Laodelphax striatellus Fallen.

As the result, for instance, compound Nos. 21 and 35 showed 100% of kill ratio at 50 ppm active ingredient.

On the other hand, as comparison, E-1 showed no killing effect at 50 ppm a.i.

## Claims

**1.** Nitro compounds of the formula (I)



(I)

wherein
$R^1$ is hydrogen, methyl, ethyl or n-propyl;
$R^2$ is hydrogen, $C_{1-4}$ alkyl, allyl, propargyl,
$C_{5-6}$ cycloalkyl optionally substituted by methyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen,
$C_{1-3}$ alkoxy of $-CH_2-Z^1$ in which
$Z^1$ is pyridyl optionally substituted by halogen;
$R^3$ is $-O-R^4$, $-S-R^4$

in which
$R^4$ is $C_{1-4}$ alkyl, allyl, $C_{3-6}$ cycloalkyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen or $-CH_2-Z^1$ in which $Z^1$ has the same meaning as stated above;
$R^5$ and $R^6$ are hydrogen, $C_{1-6}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino,methylamino, dimethylamino, methoxycarbonyl and cyano, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, $C_{1-3}$ alkoxy, hydroxy, formyl,
$C_{1-3}$ alkylamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, pyridyl optionally substituted by chlorine or methyl, or $-CH_2-Z^2$ in which $Z^2$ represents the definition of $Z^1$ hereinbefore and 5-thiazolyl optionally substituted by chlorine; in addition $R^5$ and $R^6$ may form, together with the adjacent nitrogen atom, a 3 to 6 membered cyclic group which may be substituted by methyl and may have an N, O or S atom as said ring member, besides the adjacent nitrogen atom;
and
Z is a 5-membered heterocyclic group which has one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom and may be substituted by halogen or $C_{1-4}$ alkyl, or a 6-membered heterocyclic group which has one or two nitrogen atoms and may be substituted by halogen or $C_{1-4}$ alkyl optionally substituted by halogen with the exception of the case where $R^1$ is hydrogen, methyl, ethyl or n-propyl, $R^2$ is hydrogen or $C_{1-4}$ alkyl, $R^3$ is $-S-R^4$ or

in which $R^4$ is $C_{1-4}$ alkyl, $R^5$ and $R^6$ are hydrogen or $C_{1-4}$ alkyl, and Z is 5- or 6-membered heterocyclic group having at least one nitrogen atom which may be substituted by halogen or $C_{1-4}$ alkyl optionally substituted by halogen.

**2.** The compounds according to Claim 1 wherein
$R^1$ is hydrogen, methyl or ethyl,
$R^2$ is hydrogen, methyl, ethyl, n-propyl, allyl, propargyl, cyclohexyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, $C_{1-2}$ alkoxy or
2-chloro-5-pyridylmethyl,

$R^3$ is

in which $R^5$ and $R^6$ are hydrogen, $C_{1-4}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino, methylamino, dimethylamino, methoxycarbonyl and cyano, allyl optionally substituted by chlorine, benzyl optionally substituted by chlorine,
$C_{1-2}$ alkoxy, hydroxy, formyl, $C_{1-2}$ alkylamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, 2-chloro-5-pyridyl, 2-chloro-5-pyridylmethyl or 2-chloro-5-thiazolylmethyl, in addition $R^5$ and $R^6$ may represent, together with the adjacent nitrogen atom, pyrrolidino, piperidino, 2-methylpiperidino, morpholino, piperazino or 1-isoxazolyl;
and
Z is 5-membered heterocyclic group which has one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom and may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine, or 6-membered heterocyclic group which has one or two nitrogen atoms and may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine,
with the exception of the case where $R^1$ is hydrogen, methyl or ethyl,
$R^2$ is hydrogen, methyl, ethyl or n-propyl,
$R^3$ is

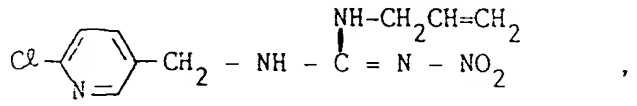
in which $R^5$ and $R^6$ are hydrogen or $C_{1-4}$ alkyl,and Z is 5- or 6-memered heterocyclic group having at least one nitrogen atom which may be substituted by halogen or $C_{1-2}$ alkyl optionally substituted by fluorine.

**3.** The compounds according to Claim 1 wherein
$R^1$ is hydrogen or methyl
$R^2$ is hydrogen, methyl, ethyl, allyl, propargyl, methoxy or 2-chloro-5-pyridylmethyl.
$R^3$ is

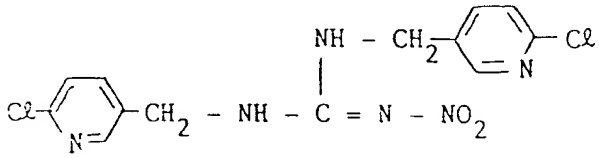
in which $R^5$ and $R^6$ are hydrogen, $C_{1-2}$ alkyl optionally substituted by at least one substituent selected from a group consisting of mercapto, methoxy, cyclohexyl, amino, methylamino, dimethylamino, methoxycarbonyl and cyano, allyl, 2-chloroallyl, benzyl, 3- or 4-chlorobenzyl, methoxy, hydroxy, formyl, methyamino, dimethylamino, amino, acetyl, benzoyl, 6-chloronicotinoyl, 2-chloro-5-pyridyl or 2-chloro-5-pyridylmethyl,
and
Z is 2-chloro-5-pyridyl,
with the exception of the case where $R^1$ is hydrogen or methyl,
$R^2$ is hydrogen, methyl or ethyl,
$R^3$ is

in which $R^5$ and $R^6$ are hydrogen
or $C_{1-2}$ alkyl, and Z is 2-chloro-5-pyridyl.

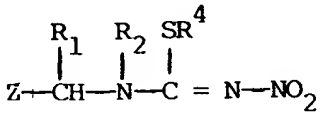
**4.** The compounds:
1-allyl-3-(2-chloro-5-pyridylmethyl)-2-nitroguanidine represented by the following formula



and
1,3-bis-(2-chloro-5-pyridylmethyl)-2-nitroguanidine represented by the following formula

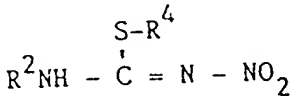


**5.** Process for the preparation of compounds of Claim 1 of the formula (Id)



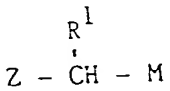
(Id)

wherein
Z, $R^1$, $R^2$ and $R^4$ have the meanings as defined in Claim 1,
characterized in that
compounds of the formula (VI)



(VI)

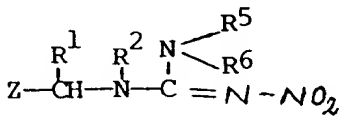
wherein $R^2$ and $R^4$ have the same meanings as mentioned above, are reacted with compounds of the formula (VII)



(VII)

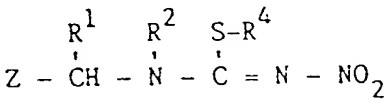
wherein $R^1$ and Z have the same meanings as mentioned above,
and M is halogen, methanesulfonyloxy or tosyloxy,
in the presence of inert solvents, and if appropriate in the presence of acid binders.

**6.** Process for the preparation of compounds of Claim 1 of the formula (Ie)



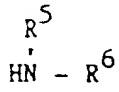
(Ie)

wherein Z, $R^1$, $R^2$, $R^5$ and $R^6$ have the meanings as defined in claim 1,
characterized, in that
compounds of the formula (Id)



(Id)

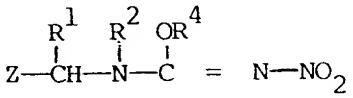
wherein $R^1$, $R^2$, $R^4$ and Z have the same meanings as defined in Claim 1,
are reacted with compounds of the formula (IV)



(IV)

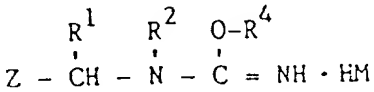
wherein $R^5$ and $R^6$ have the same meanings as mentioned above,
in the presence of inert solvents.

**7.** Process for the preparation of compounds of Claim 1 of the formula (If)



(If)

wherein Z, $R^1$, $R^2$ and $R^4$ have the meanings as defined in Claim 1,
characterized in, that
compounds of the formula (VIII)



(VIII)

wherein $R^1$, $R^2$, $R^4$, Z have the meanings as defined in Claim 1 and M is halogen, methanesulfonyloxy or tosyloxy,
are reacted with fuming nitric acid in the presence of concentrated sulfuric acid, and if appropriate in the presence of inert solvents.

**8.** Insecticidal compositions, characterised in that they contain at least one nitro compound according to Claim 1.

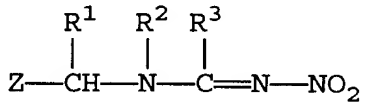
**9.** Process for combating harmful insects, characterised in that nitro compounds according to Claim 1 are allowed to act on harmful insects and/or their habitat.

**10.** Use of nitro compounds according to Claim 1 for combating harmful insects.

**11.** Process for the preparation of insecticidal compositions, characterized in that nitro compounds according to Claim 1 are mixed with extenders and/or surface-active agents.

**Patentansprüche**

**1.** Nitro-Verbindungen der Formel (I)



(I) ,

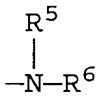
worin

$R^1$ Wasserstoff, Methyl, Ethyl oder n-Propyl ist;

$R^2$ Wasserstoff, $C_{1-4}$-Alkyl, Allyl, Propargyl, gegebenenfalls durch Methyl substituiertes $C_{5-6}$-Alkyl, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl $C_{1-3}$-Alkoxy oder $-CH_2-Z^1$ ist, worin

$Z^1$ gegebenenfalls durch Halogen substituiertes Pyridyl ist;

$R^3$ $-O-R^4$, $-S-R^4$ oder



ist, worin

$R^4$ $C_{1-4}$-Alkyl, Allyl, $C_{3-6}$-Cycloalkyl, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl oder $-CH_2-Z^1$ ist, worin $Z^1$ die oben angegebene Bedeutung hat;

$R^5$ und $R^6$ Wasserstoff, $C_{1-6}$-Alkyl, das gegebenenfalls durch wenigstens einen aus der aus Mercapto, Methoxy, Cyclohexyl, Amino, Methylamino, Dimethylamino, Methoxycarbonyl und Cyano bestehenden Gruppe ausgewählten Substituenten substituiert ist, gegebenenfalls durch Chlor substituiertes Allyl, Propargyl, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl, $C_{1-3}$-Alkoxy, Hydroxy, Formyl, $C_{1-3}$-Alkylamino, Dimethylamino, Amino, Acetyl, Benzoyl, 6-Chlornicotinyl, gegebenenfalls durch Chlor oder Methyl substituiertes Pyridyl oder $-CH_2-Z^2$ ist, worin $Z^2$ die obige Definition von $Z^1$ erfüllt und gegebenenfalls durch Chlor substituiertes 5-Thiazolyl ist; wobei zusätzlich

$R^5$ und $R^6$ zusammen mit dem benachbarten Stickstoff-Atom eine drei- bis sechsgliedrige heterocyclische Gruppe bilden können, die durch Methyl substituiert sein kann und ein N-, O- oder S-Atom als Ringglied neben dem benachbarten Stickstoff-Atom haben kann; und

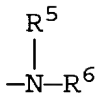
$Z$ eine fünfgliedrige heterocyclische Gruppe, die ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom hat und durch Halogen oder $C_{1-4}$-Alkyl substituiert sein kann, oder eine sechsgliedrige heterocyclische Gruppe ist, die ein oder zwei Stickstoff-Atome hat und durch Halogen oder $C_{1-4}$-Alkyl, das gegebenenfalls durch Halogen substituiert ist, substituiert sein kann,

ausgenommen den Fall, in dem

$R^1$ Wasserstoff, Methyl, Ethyl oder n-Propyl ist,

$R^2$ Wasserstoff oder $C_{1-4}$-Alkyl ist,

$R^3$ $-S-R^4$ oder



ist, worin

$R^4$ $C_{1-4}$-Alkyl ist,

$R^5$ und $R^6$ Wasserstoff oder $C_{1-4}$-Alkyl sind und

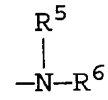
Z eine fünf- oder sechsgliedrige heterocyclische Gruppe mit wenigstens einem Stickstoff-Atom ist, die durch Halogen oder $C_{1-4}$-Alkyl, das gegebenenfalls durch Halogen substituiert ist, substituiert sein kann.

**2.** Verbindungen nach Anspruch 1, worin

$R^1$ Wasserstoff, Methyl oder Ethyl ist,

$R^2$ Wasserstoff, Methyl, Ethyl, n-Propyl, Allyl, Propargyl, Cyclohexyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, $C_{1-2}$-Alkoxy oder 2-Chloro-5-pyridylmethyl ist,

$R^3$



ist, worin

$R^5$ und $R^6$ Wasserstoff, $C_{1-4}$-Alkyl, das gegebenenfalls durch wenigstens einen aus der aus Mercapto, Methoxy, Cyclohexyl, Amino, Methylamino, Dimethylamino, Methoxycarbonyl und Cyano bestehenden Gruppe ausgewählten Substituenten substituiert ist, gegebenenfalls durch Chlor substituiertes Allyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, $C_{1-2}$-Alkoxy, Hydroxy, Formyl, $C_{1-2}$-Alkylamino, Dimethylamino, Amino, Acetyl, Benzoyl, 6-Chlornicotinyl, 2-Chlor-5-pyridyl, 2-Chlor-5-pyridylmethyl oder 2-Chlor-5-thiazolylmethyl ist, wobei zusätzlich

$R^5$ und $R^6$ zusammen mit dem benachbarten Stickstoff-Atom Pyrrolidino, Piperidino, 2-Methylpiperidino, Morpholino, Piperazino oder 1-Isoxazolyl darstellen kann; und

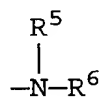
Z eine fünfgliedrige heterocyclische Gruppe, die ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom hat und durch Halogen oder $C_{1-2}$-Alkyl, das gegebenenfalls durch Fluor substituiert ist, substituiert sein kann, oder eine sechsgliedrige heterocyclische Gruppe, die ein oder zwei Stickstoff-Atome hat und durch Halogen oder $C_{1-2}$-Alkyl, das gegebenenfalls durch Fluor substituiert ist, substituiert sein kann,

ausgenommen den Fall, in dem

$R^1$ Wasserstoff, Methyl oder Ethyl ist,

$R^2$ Wasserstoff, Methyl, Ethyl oder n-Propyl ist,

$R^3$



ist, worin

$R^5$ und $R^6$ Wasserstoff oder $C_{1-4}$-Alkyl sind und

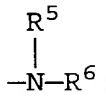
Z eine fünf- oder sechsgliedrige heterocyclische Gruppe mit wenigstens einem Stickstoff-Atom ist, die durch Halogen oder $C_{1-2}$-Alkyl, das gegebenenfalls durch Fluor substituiert ist, substituiert sein kann.

**3.** Verbindungen nach Anspruch 1, worin

$R^1$ Wasserstoff oder Methyl ist,

$R^2$ Wasserstoff, Methyl, Ethyl, Allyl, Propargyl, Methoxy oder 2-Chloro-5-pyridylmethyl ist,

$R^3$



ist, worin

$R^5$ und $R^6$ Wasserstoff, $C_{1-2}$-Alkyl, das gegebenenfalls durch wenigstens einen aus der aus Mercapto, Methoxy, Cyclohexyl, Amino, Methylamino, Dimethylamino, Methoxycarbonyl und Cyano bestehenden Gruppe ausgewählten Substituenten substituiert ist, Allyl, 2-Chlorallyl, Benzyl, 3- oder 4-Chlorbenzyl, Methoxy, Hydroxy, Formyl, Methylamino, Dimethylamino, Amino, Acetyl, Benzoyl, 6-Chlornicotinyl, 2-Chlor-5-pyridyl oder 2-Chlor-5-pyridylmethyl ist, und

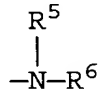
Z 2-Chlor-5-pyridyl ist,

ausgenommen den Fall, in dem

$R^1$ Wasserstoff oder Methyl ist,

$R^2$ Wasserstoff, Methyl oder Ethyl ist,

$R^3$



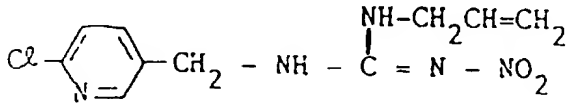
ist, worin

$R^5$ und $R^6$ Wasserstoff oder $C_{1-2}$-Alkyl sind und

Z 2-Chlor-5-pyridyl ist.

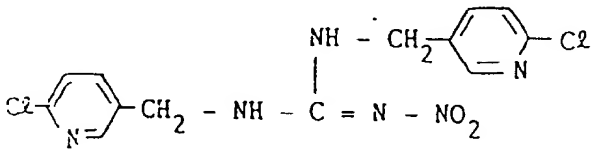
**4.** Verbindungen

1-Allyl-3-(2-chlor-5-pyridylmethyl)-2-nitroguanidin, dargestellt durch die folgende Formel

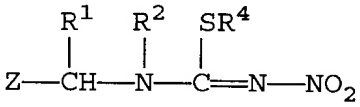


und

1,3-Bis-(2-chlor-5-pyridylmethyl)-2-nitroguanidin, dargestellt durch die folgende Formel

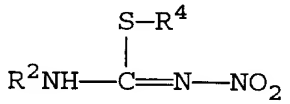


**5.** Verfahren zur Herstellung von Verbindungen nach Anspruch 1 der Formel



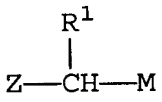
(Id) ,

worin
Z, $R^1$, $R^2$ und $R^4$ die in Anspruch 1 angegebenen Bedeutungen haben, dadurch gekennzeichnet, daß Verbindungen der Formel (VI)



(VI)

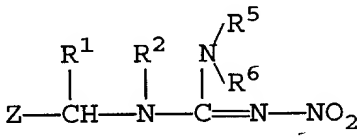
in der $R^2$ und $R^4$ die oben angegebenen Bedeutungen haben, mit Verbindungen der Formel (VII)



(VII) ,

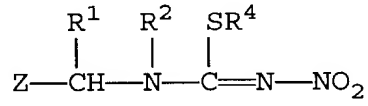
in der $R^1$ und Z die oben angegebenen Bedeutungen haben und
M Halogen, Methansulfonyloxy oder Tosyloxy ist,
in Gegenwart inerter Lösungsmittel und gegebenenfalls in Gegenwart säurebindender Mittel umgesetzt werden.

**6.** Verfahren zur Herstellung von Verbindungen nach Anspruch 1 der Formel



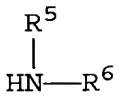
(Ie) ,

worin
Z, $R^1$, $R^2$, $R^5$ und $R^6$ die in Anspruch 1 angegebenen Bedeutungen haben, dadurch gekennzeichnet, daß Verbindungen der Formel (Id)



(Id) ,

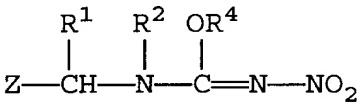
worin
$R^1$, $R^2$, $R^4$ und Z die in Anspruch 1 angegebenen Bedeutungen haben, mit Verbindungen der Formel (IV)



(IV) ,

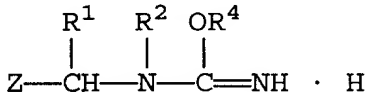
in der $R^5$ und $R^6$ die oben angegebenen Bedeutungen haben, in Gegenwart inerter Lösungsmittel umgesetzt werden.

**7.** Verfahren zur Herstellung von Verbindungen nach Anspruch 1 der Formel



(If) ,

worin
Z, $R^1$, $R^2$ und $R^4$ die in Anspruch 1 angegebenen Bedeutungen haben, dadurch gekennzeichnet, daß Verbindungen der Formel (VIII)



(VIII) ,

worin
$R^1$, $R^2$, $R^4$, Z die in Anspruch 1 angegebenen Bedeutungen haben und M Halogen, Methansulfonyloxy oder Tosyloxy ist, mit rauchender Salpetersäure in Gegenwart von konzentrierter Schwefelsäure und gegebenenfalls in Gegenwart inerter Lösungsmittel umgesetzt werden.

**8.** Insektizide Zusammensetzungen, dadurch gekennzeichnet, daß sie wenigstens eine Nitro-Verbindung gemäß Anspruch 1 enthalten.

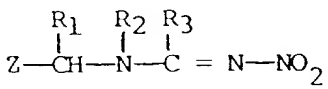
**9.** Verfahren zur Bekämpfung schädlicher Insekten, dadurch gekennzeichnet, daß man Nitro-Verbindungen gemäß Anspruch 1 auf schädliche Insekten und oder deren Lebensraum einwirken läßt.

**10.** Verwendung von Nitro-Verbindungen gemäß Anspruch 1 zur Bekämpfung schädlicher Insekten.

**11.** Verfahren zur Herstellung insektizider Zusammensetzungen, dadurch gekennzeichnet, daß Nitro-Verbindungen gemäß Anspruch 1 mit Streckmitteln und/oder oberflächenaktiven Mitteln vermischt werden.

**Revendications**

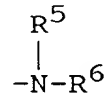
**1.** Composés nitrés de formule (I)



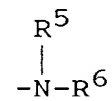
(I)

dans laquelle
$R^1$ représente l'hydrogène, un groupe méthyle, éthyle ou n-propyle ;
$R^2$ représente l'hydrogène, un groupe alkyle en $C_{1-4}$, allyle, propargyle, cycloalkyle en $C_{5-6}$ facultativement substitué par un radical méthyle, un groupe phényle fácultativement substitué par un halogène, un groupe benzyle facultativement substitué par un halogène, un radical alkoxy en $C_{1-3}$ ou $-CH_2-Z^1$ dans lequel

$Z^1$ est un groupe pyridyle facultativement substitué par un halogène ;
$R^3$ est un groupe $-O-R^4$, $-S-R^4$ ou

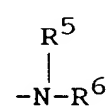


dans lequel
$R^4$ est un groupe alkyle en $C_{1-4}$, allyle, cycloalkyle en $C_{3-6}$, phényle facultativement substitué par un halogène, benzyle facultativement substitué par un halogène, ou un radical $-CH_2-Z^1$ dans lequel $Z^1$ a la même définition que ci-dessus ;
$R^5$ et $R^6$ représentent de l'hydrogène, un groupe alkyle en $C_{1-6}$ portant facultativement au moins un substituant choisi dans le groupe des substituants mercapto, méthoxy, cyclohexyle, amino, méthylamino, diméthylamino, méthoxycarbonyle et cyano, un groupe allyle facultativement substitué par du chlore, un groupe propargyle, phényle facultativement substitué par du chlore, benzyle facultativement substitué par du chlore, un groupe alkoxy en $C_{1-3}$, hydroxyle, formyle, alkylamino en $C_{1-3}$, diméthylamino, amino, acétyle, benzoyle, 6-chloronicotinoyle,pyridyle facultativement substitué par du chlore ou un radical méthyle, ou un radical $-CH_2-Z^2$ dans lequel $Z^2$ représente la définition donnée ci-dessus pour $Z^1$ et un groupe 5-thiazolyle facultativement substitué par du chore ; en outre, $R^5$ et $R^6$ peuvent former, conjointement avec l'atome adjacent d'azote, un groupe cyclique de 3 à 6 chaînons qui peut être substitué par un radical méthyle ou peut avoir un atome d'azote, d'oxygène ou de soufre comme chaînons du noyau, outre l'atome adjacent d'azote ; et
Z est un groupe hétérocyclique pentagonal qui comprend un ou deux atomes d'azote, ou un atome d'azote et ou bien un atome d'oxygène ou bien un atome de soufre et peut être substitué par un halogène ou un radical alkyle en $C_{1-4}$, ou un groupe hétérocyclique hexagonal qui comprend un ou deux atomes d'azote et peut être substitué par un halogène ou un radical alkyle en $C_{1-4}$ facultativement substitué par un halogène,
à l'exception du cas où $R^1$ est l'hydrogène, un groupe méthyle, éthyle ou n-propyle, $R^2$ est l'hydrogène ou un groupe alkyle en $C_{1-4}$, $R^3$ est un groupe $-S-R^4$ ou



dans lequel $R^4$ est un radical alkyle en $C_{1-4}$, $R^5$ et $R^6$ sont de l'hydrogène ou des radicaux alkyle en $C_{1-4}$, et Z est un groupe hétérocyclique pentagonal ou hexagonal comprenant au moins un un atome d'azote qui peut être substitué par un halogène ou par un radical alkyle en $C_{1-4}$ facultativement substitué par un halogène.

**2.** Composés suivant la revendication 1, dans lesquels
$R^1$ est l'hydrogène, un groupe méthyle ou éthyle,
$R^2$ est l'hydrogène, un groupe méthyle ou éthyle, n-propyle, allyle, propargyle, cyclohexyle, phényle facultativement substitué par du chlore, benzyle facultativement substitué par du chore, alkoxy en $C_1$ ou $C_2$ ou 2-chloro-5-pyridylméthyle,
$R^3$ est un groupe



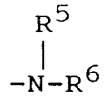
dans lequel $R^5$ et $R^6$ sont de l'hydrogène, des groupes alkyle en $C_{1-4}$ portant facultativement au moins un substituant choisi dans le groupe des substituants mercapto, méthoxy, cyclohexyle, amino, méthylamino, diméthylamino, méthoxycarbonyle et cyano, un groupe allyle facultativement substitué par du chlore, un groupe benzyle facultativement substitué par du chlore, un groupe alkoxy en $C_1$ ou $C_2$ ,

hydroxy, formyle, alkyleamino en $C_1$ ou $C_2$, diméthylamino, amino, acétyle, benzoyle, 6-chloronicotinoyle, 2-chloro-5-pyridyle, 2-chloro-5-pyridylméthyle ou 2-chloro-5-thiazolylméthyle, en outre $R^5$ et $R^6$ peuvent représenter, conjointement avec l'atome adjacent d'azote, un groupe pyrrolidino, pipéridino, 2-méthylpipéridino, morpholino, pipérazino ou 1-isoxazolyle ;

Z est un groupe hétérocyclique pentagonal qui comprend 1 ou 2 atomes d'azote ou un atome d'azote et ou bien un atome d'oxygène ou bien un atome de soufre et peut être substitué par un halogène ou un radical alkyle en $C_1$ ou $C_2$ facultativement substitué par du fluor, ou un groupe héterocyclique hexagonal qui comprend un ou deux atomes d'azote et peut être substitué par un halogène ou un radical alkyle en $C_1$ ou $C_2$ facultativement substitué par du fluor, à l'exception du cas ou $R^1$ est l'hydrogène, un groupe méthyle ou éthyle,

$R^2$ est l'hydrogène, un groupe méthyle, éthyle ou n-propyle,

$R^3$ est un groupe



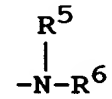
dans lequel $R^5$ et $R^6$ sont de l'hydrogène ou des radicaux alkyle en $C_{1-4}$ et Z est un groupe hétérocyclique pentagonal ou hexagonal ayant au moins un atome d'azote qui peut être substitué par un halogène ou un radical alkyle en $C_1$ ou $C_2$ facultativement substitué par du fluor.

**3.** Composés suivant la revendication 1, dans lesquels

$R^1$ est l'hydrogène ou le groupe méthyle.

$R^2$ est l'hydrogène, un groupe méthyle, éthyle, allyle, propargyle, méthoxy ou 2-chloro-5-pyridylméthyle,

$R^3$ est un groupe

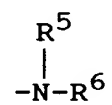


dans lequel $R^5$ et $R^6$ représentent l'hydrogène, des groupes alkyle en $C_1$ ou $C_2$ portant facultativement au moins un substituant choisi dans le groupe des substituants mercapto, méthoxy, cyclohexyle, amino, méthylamino, diméthylamino, méthoxycarbonyle et cyano, un groupe allyle, 2-chlorallyle, benzyle, 3- ou 4-chlorobenzyle, méthoxy, hydroxy, formyle, méthylamino, diméthylamino, amino, acétyle, benzoyle, 6-chloronicotinoyle, 2-chloro-5-pyridyle ou 2-chloro-5-pyridylméthyle,

Z est un groupe 2-chloro-5-pyridyle,

à l'exception du cas où $R^1$ est l'hydrogène ou un groupe méthyle, $R^2$ est l'hydrogène, un groupe méthyle ou éthyle,

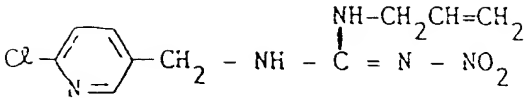
$R^3$ est un groupe



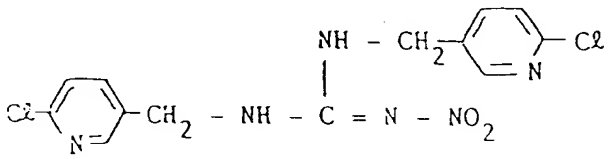
dans lequel $R^5$ et $R^6$ représentent l'hydrogène ou un groupe alkyle en $C_1$ ou $C_2$ et Z est un groupe 2-chloro-5-pyridyle.

**4.** Les composés :

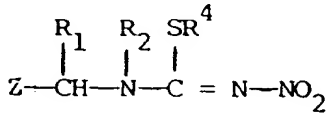
1-allyl-3-(2-choro-5-pyridylméthyl)-2-nitroguanidine représenté par la formule :



1,3-bis-(2-chloro-5-pyridylméthyl)-2-nitroguanidine représenté par la formule :

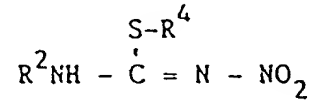


**5.** Procédé de production de composés suivant la revendication 1 de formule (Id):



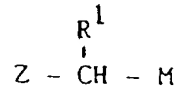
(Id)

dans lequel
Z, $R^1$, $R^2$ et $R^4$ ont les définitions données dans la revendication 1,
caractérisé en ce qu'on fait réagir des composés de formule (VI)



(VI)

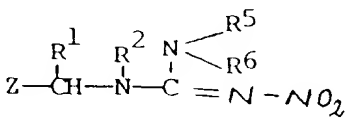
dans laquelle $R^2$ et $R^4$ ont les mêmes définitions que ci-dessus,
avec des composés de formule (VII)



(VII)

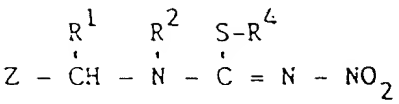
dans laquelle $R^1$ et Z ont les mêmes définitions que ci-dessus
et M est un halogène, un groupe méthanesulfonyloxy ou tosyloxy,
en présence de solvants inertes et, le cas échéant, en présence d'accepteurs d'acides.

**6.** Procédé de production de composés suivant la revendication 1 de formule (Ie) :



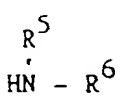
(Ie)

dans laquelle Z, $R^1$, $R^2$, $R^5$ et $R^6$ ont les définitions données dans la revendication 1,
caractérisé en ce qu'on fait réagir des composés de formule (Id) :



(Id)

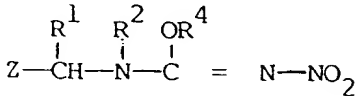
dans laquelle $R^1$, $R^2$, $R^4$ et Z ont les définitions données dans la revendication 1, avec des composés de formule (IV)



(IV)

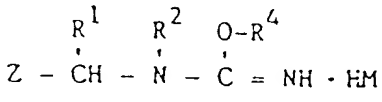
dans laquelle $R^5$ et $R^6$ ont les définitions mentionnées ci-dessus, en présence de solvants inertes.

**7.** Procédé de production de composés suivant la revendication 1 de formule (If) :



**(If)**

dans laquelle Z, $R^1$, $R^2$ et $R^4$ ont les définitions données dans la revendication 1, caractérisé en ce qu'on fait réagir des composés de formule (VIII)



(VIII)

dans laquelle $R^1$, $R^2$, $R^4$, Z ont les définitions données dans la revendications 1 et M est un halogène, un groupe méthanesulfonyloxy ou tosyloxy,
avec l'acide nitrique fumant en présence d'acide sulfurique concentré, et le cas échéant en présence de solvants inertes.

**8.** Compositions insecticides, caractérisées en ce qu'elles contiennent au moins un composé nitré suivant la revendication 1.

**9.** Procédé pour combattre des insectes nuisibles, caractérisé en ce qu'on fait agir des composés nitrés suivant la revendication 1 sur des insectes nuisibles et/ou sur leur habitat.

**10.** Utilisation de composés nitrés suivant la revendication 1 pour combattre des insectes nuisibles.

**11.** Procédé de préparation de compositions insecticides, caractérisé en ce qu'on mélange des composés nitrés suivant la revendication 1 avec des diluants et/ou des agents tensio-actifs.